Esterification of Bio-oil to Bio-diesel by Using Long Chain Alcohol with Present of Acid Catalyst

by

Wan Mohd Syafiq Bin Wan Ismail

Dissertation submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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Approved by,

(AP. Dr. Suzana Yusup)

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TRONOH, PERAK
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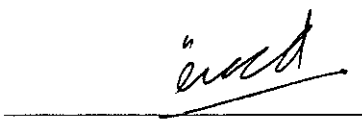
CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



WAN MOHD SYAFIQ BIN WAN ISMAIL

ABSTRACT

The liquid product from pyrolysis of bio-mass which is bio-oil cannot be used in refinery without further upgrading. However, its heavy fraction, mixed with aromatic hydrocarbon was considered as a potential for esterification feedstock. Limited study was done to conduct esterification using pyrolysis bio-oil. Most method of esterification was using methanol react with based catalyst. This method results in a high yield of bio-diesel in short time. However, is limited to relatively clean vegetable oil and formation of soaps and emulsions make it hard to clean. Using acid catalyst such as sulphuric acid with 1-butanol, give more advantage to the process. It seems more economical because high yield of organic liquid product produce using small amount of catalyst and alcohol. Beside the reaction time is shorter when using long chain of alcohol. The highest production yield of organic liquid product was achieved at 58 wt% at parameter 60 minutes of reaction time, at temperature 90 ^{o}C, alcohol molar ratio to bio-oil is 3:1 and at 2 wt% of catalyst. Comparative study have been conducted in order to identify any different from organic liquid product with commercial diesel.

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TABLE OF CONTENT

LIST OF TABLE

LIST OF FIGURE

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Renewable energy is growing importance and it relate to the environment and security of energy supply. Ever since environmental concerns over the fossil fuels with respect to their limited reserves emerged, interest in environmental friendly alternative energy resources that can reduce dependency on fossil fuels has been growing. With respect to the global issues of sustainable energy and reduction in greenhouse gases, bio-oil is getting increased attention as a potential source of renewable energy.

Particularly, bio-oil is seen to play an important role both as chemical feedstock and as alternative to fossil fuels. Due to these facts, investigations on thermo-chemical and bio-chemical conversion technologies for bio-oil utilization have been conducted worldwide.

Bio-oil has some advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. Bio-oils also referred to as biomass pyrolysis liquids, pyrolysis oils, or bio-crude oils, are dark brown, free flowing liquids with an acrid or smoky odour (Anja Oasmaa *et al.*, 2009). They are complex mixtures of compounds that are derived from the depolymerisation of cellulose, hemicelluloses and lignin.

Chemically, they comprise quite a lot of water, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds. Bio-oils have been regarded as promising candidates to replace petroleum fuels to be used in various thermal devices.

Esterification is chemical process of making ester, which are compounds of chemical structure R-COOR', where R and R' are either alkyl or aryl groups (March J., 1992). The classic synthesis is the Fischer esterification, which involves treating a carboxylic acid with an alcohol in the presence of dehydrating agent:

$$RCO_2H + R'OH \leftrightarrow RCO_2R' + H_2O$$

Biodiesel is composed if alkyl esters of fatty acid. These fatty acid esters are typically synthesized by the transesterification of triacylglycerides from seed oil with short chain alcohol like methanol using either based or acid catalyst.

In the typical commercial process, biodiesel is synthesized from vegetable oil and methanol using based catalyst, such as sodium hydroxide (Bradley D. Wahlen *et. al.,* 2008). This method results in high yields of biodiesel in a relatively short time. However this method is limited to relatively clean vegetable oils containing very low concentration of free fatty acid which is less than 0.5 % (Bradley D. Wahlen *et. al.,* 2008). The presence of free fatty acids above this quantity in the oils results in the formation of soap and emulsions, which is complicate the washing of the biodiesel and removal of glycerol.

Presence of alcohol is must in esterification process. There are limited studies that conduct the esterification process by using high chain of alcohol such as n-butanol. Most of the experiments were set up using methanol and ethanol. Mahfud F. H. *et. al.* (2007) have proved in his research that by upgrading bio-oil with a high boiling alcohol like n-butanol in the presence of acid catalyst can continuously remove water from the reaction medium, and the desired reactions (esterification and acetalisation) are driven to completion. Using this approach, the water content of the pyrolysis oil is reduced significantly and values less than 5 wt% were obtained using sulphuric acid.

1.2 Problem Statement

Bio-fuels have become an attractive alternative fuel because of their possible environmental benefits and the current concern over the depletion of fossil fuel sources. The demand for bio-fuels will rise in the future due to the rise in the price of fossil fuel, energy security reasons, environmental and economical issues. The using of bio-fuel as an alternative for fossil fuel will help to prevent environment pollution and green house effect. Although biomass contains carbon and the generation of energy out of this fuel releases CO2, this CO2 is also taken out of the atmosphere during growth of the plant.

Most of biodiesel currently being produced is mainly dependent on edible source such as soybean oil and palm oil. Other sources were researched in order to find alternative raw material for the process but most of which cannot compete with the ready availability of large stocks of edible oils. The usage of agriculture waste to produce bio-oil via pyrolysis process seems promise the alternative of using cooking oil. Using agriculture waste such as empty fruit bunch (EFB) or palm kernel shell (PKS) to produce bio-oil can help to reduce agriculture solid waste and turn into something valuable. The continuous feed stock of EFB and PKS also promise the continuous production of bio-oil that later will be upgrade to bio-diesel.

Limited research on using long chain alcohol for esterification, give motivation to conduct this research. The esterification process on this study will be carried out using rotary evaporation as close batch system at highest optimum process based on recent studies. By determining and justifying the product, as bio-diesel or butyl-ester. Later, this project can declare that the process that been developed is functioning and have a potential to be commercialize. Temperature, reaction time, ratio of alcohol to bio-oil and amount of catalyst played major role in determining the fraction of yield of bio-diesel production.

1.3 Objectives

The main objective of this experiment is to investigate the production yield of bio-diesel at optimum process parameter by using n-butanol as selected alcohol. Besides that, to compare the production yield and effect of using high concentration acid catalyst with base catalyst. Also need to characterize the properties of organic liquid product (OLP) and compare it with bio-oil and commercial petroleum diesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Bio-diesel Alternative Fuel

The search for alternative fuels is an ongoing research enterprise. The combustion of fossil-based fuels is a one-way process which will eventually exhaust the available stocks of raw petroleum materials and add significantly to the amount of carbon dioxide in the atmosphere. The potential consequences of both activities will probably still be argued long after it is too late to do anything about them.

A good alternative fuel would ideally come from renewable resources, be energy-rich, green in production and be at least carbon-neutral. This last requirement means that no new carbon would be released into the environment during combustion. Plant-based fuels meet this criterion because the carbon dioxide (CO_2) which plants consume from the atmosphere is returned when the plant material combusts. If only part of the plant is burned, then the process might actually be better than carbon-neutral, assuming the remaining plant material is used in some other form that sequesters the carbon and prevents its return to the atmosphere, and that manufacturing processes are not fuel-intensive. There are certainly other issues associated with the widespread use of plant-based bio-fuels, not the least of which is the resources like water and arable land which such crops might take from needed food production.

A lot of attention has been devoted in the popular press recently to a fuel called bio-diesel. An internet search under this term will yield a spectacular number of hits that range from government reports to home-brew recipes touted by those who now run their vehicles on fuel they produce from vegetable oil. It turns out that bio-diesel fuel is amazingly simple to make, rather green, and could be carbon-neutral. Its energy content is one of the things this experiment is about.

The diesel engine was designed by Rudolph Diesel in 1895 as an alternative to the standard internal combustion engine that powers most of our cars (Sharma, R. K. and Bakhshi, N. N., 1993). It could run on less refined hydrocarbon mixtures that ignite upon compression and therefore required no spark. The first diesel engines were actually designed to run on vegetable oil but petroleum diesel was available as a cheap by-product of gasoline production and was less viscous than vegetable oil so the engines were eventually redesigned for it (Paul G.B. and Randy D.C., 2008).

2.1.1 Advantages of Bio-diesel

Unlike petroleum diesel that contains hydrocarbon, bio-diesel consists of a mixture of monoalkyl esters of long chain fatty acids. These are typically produced by esterification (Anton A. K. *et. al.*, 2008).

Bio-diesel has several advantages over petroleum diesel. It is safe, renewable, non-toxic and bio-degradable. It contains no sulphur and is a better lubricant (Blumberg K. O., *et. al.*, 2003). Despite the chemical differences, these two fuels have similar properties and performance parameter. Table 2.1 show the fuel property different between diesel and bio-diesel.

Table 2.1: Petroleum diesel vs. bio-diesel (Anton A. K. *et. al.*, 2008)

Fuel Property	Diesel	Bio-Diesel
Fuel Composition	$C_{10} - C_{21}$ HC[a]	$C_{12} - C_{22}$FAME[a]
Kinetic Viscosity, mm^2/s	1.3 – 4.1	1.9 – 6.0
Specific Gravity, kg/L	0.85	0.88
Boiling Point, °C	188 – 343	182 – 338
Flash Point, °C	60 - 80	100 – 170
Pour Point, °C	-35 to -15	-15 to 10
Cetane Number	40 - 55	48 – 65

An important characteristic of diesel fuels is the ability to auto ignites, quantified by cetane number. Bio-diesel not only has higher cetane number than petroleum diesel but also has higher flash point, meaning better and safer

performance. Remarkably, bio-diesel is the only alternative fuel currently available with an overall positive life cycle energy balance. Another significant advantage of biodiesel is its low emission profile and its oxygen content of 10-11%. Biodiesel is called the environmentally friendly bio-fuel since it provides a means to recycle carbon dioxide. In other words, biodiesel does not contribute to global warming (Edgar L *et. al.,* 2005).

2.2 Biomass: Continuous Feedstock

Biomass is recognised as an important source of energy, particularly in developing countries where it may be used to reduce the reliance on imported forms of energy and conserve the limited supplies of fossil fuels. Developing countries tend to have economies largely based on agriculture and forestry. Agricultural waste is one form of biomass which is readily available but is largely not utilised in energy recovery schemes.

A principal advantage of biomass is its low greenhouse gas emission characteristic. Biomass does not spew carbon dioxide (CO_2) into the atmosphere as it absorbs an equal amount of carbon in growing as it releases when consumed as a fuel. Biomass contains less sulphur than coal, and consequently produces less sulphur dioxide (SO_2)

Biomass can be simply defined as by product with no or low profit generated from agricultural or industrial processes. Main sources of biomass in Malaysia can be defined as domestic waste, agricultural residues waste, animal wastes and wood chips. Among this category, agricultural residues waste contribute 85.5 % of total waste per annum, where 94 % or equivalent to 80 million tonnes annually wastes are from palm oil industry (Mohamed A. H. and Shahrakbah Y., 2009).

There several ways of technologies to produce bio-oil from biomass. But recently most bio-oil was produce via pyrolysis process through fluidized bed reactor. The difference in bio-oil production yield from pyrolysis depends on the amount of ash in the virgin biomass and relative amounts of lignin and cellulose. A

high lignin content in bark or nut shells depress the bio-oil yield and a high cellulose content in paper waste enhances the bio-oil yield (Weerachanhai P. *et. al.*, 2009).

2.3 Upgrading Bio-oil to Bio-diesel via Esterification

Bio-diesel is the methyl or ethyl ester of the fatty acids found in vegetable oils or animal fats. At the simplest, these fats are triglycerides. That means some rather large carboxylic acids have formed a triple ester with the glycerol molecule (March J., 1992). This makes for a very viscous liquid because the strands of the fat get tangled with each other. To reduce the viscosity it is possible to detach the glycerol molecule and replace it with methanol at each strand of fatty acid. The process is known as transesterification and can be catalyzed by either acid or base (Sven S. and Jurgen G., 2003). Because potential acid residues are not friendly to metal engine parts and because the process is faster with the base catalyst, sodium or potassium hydroxide is generally used along with methanol to treat the vegetable oil.

Generally esterification is the chemical process for making esters, which are compounds of the chemical structure R-COOR', where R and R' are either alkyl or aryl groups. The most common method for preparing esters is to heat a carboxylic acid, R-CO-OH, with an alcohol, R'-OH, while removing the water that is formed (March J., 1992). A mineral acid catalyst is usually needed to make the reaction occur at useful rate.

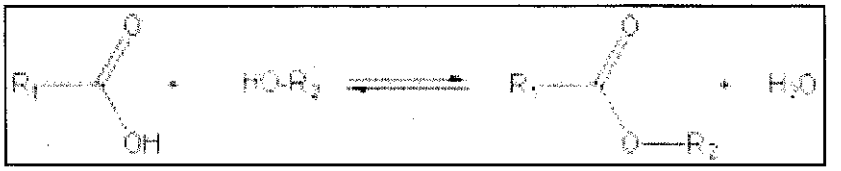

Figure 2.1: Reaction of esterification (March J., 1992).

The equilibrium constant for such reactions is about 5 for typical ester example ethyl acetate (Roger J. W. *et. al.*, 1982). But the reaction is slow in the absence of a catalyst. Common catalyst use for esterification reaction is Sulphuric Acid (H_2SO_4). Many other acids are also used such as polymeric sulfonic acids.

Since esterification is highly reversible, the yield of the ester can be improved using Le Chatelier principle:

- Using the alcohol in large excess as a solvent.
- Using a dehydrating agent such as H_2SO_4, not only catalyzes the reaction but sequesters water.
- Removal of water by physical means such as distillation as low boiling azeotropes with toluene.

Based on LeChâtelier's Principle, we know that increasing the amount of either of the reactants should help (Sven S. and Jurgen G., 2003). If either the alcohol or acid is considerably less expensive this is one possible approach. Under the right experimental conditions it is also possible to remove water as refluxing is taking place. The disappearance of a product will tend to the reaction to the right. However, in laboratory scale organic synthesis the usual aim is not so much getting a lot of product as it is determining how the product forms and how it can be isolated, purified and identified.

2.3.1 Homogeneous Base Catalyst Esterification

The esterification reaction requires a catalyst in order to obtain reasonable conversion rates. The nature of the catalyst is fundamental since it determines the compositional limits that the feedstock must conform to. Furthermore, the reaction conditions and post separation steps are predetermined by the nature of the catalyst used. Currently, most biodiesel is prepared using alkaline catalysts, such as sodium and potassium hoxides and hydroxides. Industrially, sodium hydroxide (NaOH) and potassium hydroxide (KOH) are preferred due to their wide availability and low cost (Edgar L *et. al.*, 2005).

Even though esterification is feasible using homogenous base catalysts, the overall base catalyzed process suffers from serious limitations that translate into high production cost for bio-diesel. Bradley D. Wahlen *et. al.* (2008) stated that, strict feedstock specifications are a main issue with this process. In particular, the total free fatty acid (FFA) content associated with the lipid feedstock must not exceed 0.5

wt%. otherwise, soap formation seriously hinders the production of fuel grade bio-diesel. Mahfud F. H. *et. al.* (2007) have stated in his research that, soap forms when the metal hydroxide catalyst react with FFAs in the feedstock. Soap productions give rise to the formation of gels, increase viscosity and greatly increases product separation cost (Hanna M. A and Ma F. R., 1999).

The factors in favour and against for based catalyzed trans-esterification are assembled in Table 2.2.

Table 2.2: Factors for and against base catalyzed trans-esterification reaction (Edgar L *et. al.,* 2005).

Factors for	**Factors against**
1. Approximately 4000 times faster than acid catalysed trans-esterification. 2. The FFA content of the oil should be as low as possible. 3. Methoxides are more effective than hydroxides.	1. Glycerides and alcohol must be substantially anhydrous, otherwise leads to saponification, which reduces the catalytic efficiency, forms gels and causes difficulty in separation of glycerol. 2. The molar ratio of alcohol has to be 6:1 or higher instead of 3:1.

Though base catalyzed trans-esterification reaction is fast, the main advantages include energy intensiveness, difficult in separting the glycerol from alkyl-ester. Alkaline waste water requires treatment and FFA and water interfere with the trans-esterification of triglycerides both in aqueous and non-aqueous conditions.

The soap causes processing problem downstream in the product separation because emulsion formation. Usually, this problem is overcome through a previous esterification step where FFA are firstly esterified to fatty acid methyl ester (FAME) using homogeneous acid catalyst, and then once acid homogeneous catalyst has been removed, trans-esterification of triglycerides is performed as usual by means of an alkaline catalyst concentration (Juan A. Melero *et. al.,* 2009).

2.3.2 Homogeneous Acid Catalyzed Reactions

The demanding feedstock specifications for base catalyzed reactions have led researchers to seek catalytic and processing alternatives that could ease this difficulty and lower production costs. Methodologies based on acid catalyzed reactions have the potential to achieve this since acid catalysts do not show measurable susceptibility to FFA.

The liquid acid-catalyzed trans-esterification process does not enjoy the same popularity in commercial applications as its counterpart, the base catalyzed process. The fact that the homogeneous acid catalyzed reaction is about 4000 times slower than the homogeneous base catalyzed reaction has been one of the main reasons (Srivasta A. and Prasad R., 2000).

However, acid-catalyzed trans-esterifications hold an important advantage with respect to base catalyzed ones, the performance of the acid catalyst is not strongly affected by the presence of FFA in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and trans-esterification. Thus, a great-advantage with acid catalysts is that they can directly produce biodiesel from low cost lipid feedstocks, generally associated with high FFA concentration (Juan A. Melero *et. al.*, 2009).

The acids employed for trans-esterification include sulphuric acid, phosphoric acid, hydrochloric acid and organic sulphonic acids. The factors favourable and disadvantages of homogeneous acid catalysts for trans-esterification are given in Table 2.3.

Table 2.3: Favourable and disadvantages factors for homogeneous acid catalyzed trans-esterification (Edgar L *et. al.*, 2005).

Favourable factors	Disadvantageous factors
1. Trans-esterification can be carried out at high fatty acid content and more water. 2. Acid catalyst is preferred when oil component is low grade material like sulphur olive oil. 3. The extraction and trans-esterification proceed simultaneously. This avoids the use of pre-extracted seed oil.	1. The trans-esterification reaction is slower than that of catalyst by base.

Homogeneous acids such as sulphuric acid, hydrochloric acid, nitric acid, and several others can be used to catalyze esterification. When using a homogenous acid catalyst for the esterification of FFA in the presence of triglycerides, the catalyst can be recovered in the methanol layer and re-used. Several variables, however, may affect the recoverability and re-use of the catalyst (Matthew B. B. *et. al.*, 2008).

For example, if trans-esterification of triglycerides takes place simultaneously during esterification of FFA, a glycerol layer can form and may result in the loss of the acid catalyst. A study by Goff and Suppes (2004) reported acid catalyzed trans-esterification when sulphuric acid was used as a catalyst, however when other acids were used a glycerol layer was not formed; there was no report, however, of how much catalyst was recovered.

2.4 Sulphuric Acid as Acid Catalyst

Sulphuric acid is a highly corrosive strong mineral acid with the molecular formula H_2SO_4. The historical name of this acid is oil of vitriol. The sulphuric acid is a colourless to slightly yellow liquid which is clear or viscous and is soluble in water at all concentrations. It is a dibasic acid. The corrosiveness of it is mainly

due to its strong acidic nature, strong dehydrating property and if concentrated strong oxidizing property (March J., 1992).

Table 2.4: Chemical and physical properties of 95 – 97% H_2SO_4 (Wikipedia-sulfuric acid, 2011)

Properties	**Value**
Density (kg/L)	1.83
Concentration (mol/L)	~ 18
Molar mass (g/mol)	98.079
Melting point (°C)	10
Boiling point (°C)	337
Acidity (pK_a)	-3, 1.99
Viscosity (cP)	26.7

High concentrated H_2SO_4 must be handling with care, and proper protective equipment (PPE) should be use all time.

Matthew B. B. *et. al.* (2008), have prove that H_2SO_4 are more sensitive to water compare to hydrochloric acid (HCl). It was found that HCl exhibits a higher tolerance for accumulating water in the methanol layer. After H_2SO_4 was recovered and re-used, the observed rate constant decreased more than 50 % to a value comparable to that observed for HCl at more than three times the water concentration.

Donato A. G. *et. al.* (2008), have shown that sulphuric acid and methanesulfonic acid were the best catalyst, with conversions higher than 90 % at 60 minutes of reaction and with alcohol (methanol) molar ratio to FFA is 1:3 at desired temperature of 130 °C. The result may be assigned to the higher acid strength. Higher acid strength means more H^+ species been released to protonate the carboxylic moiety of the fatty acid, increasing the electrophilicity of the carbonyl carbon atom and facilitating the second step, which is the nucleophilic attack of the alcohol, forming a tetrahedral intermediate (Lotero E. *et. al.*, 2005).

2.5 Advantages of Long Chain Alcohol

The present of alcohol in esterification process as solvent, is to break the fatty acid chain to produce alkyl ester group and water. Bio-diesel is composed of alkyl ester of fatty acids. These fatty acid esters are typically synthesized by the trans-esterification with a short chain alcohol such as methanol or ethanol.

The researchers say the long chained alcohol delivers more energy, does not corrode the engine and is more compatible with jet fuel or diesel (Bradley D. Wahlen *et. al.,* 2008). Ethanol, one of the leading sources of bio-fuel, contains just two carbon atoms and the most common naturally produced long chain alcohols contain no more than five carbon atoms.

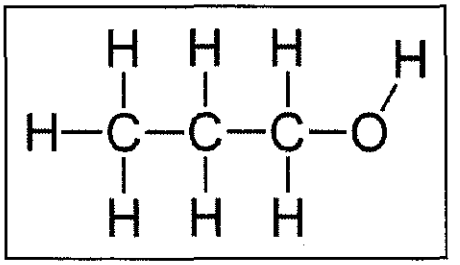

Figure 2.2: 1-propanol chain (Wikipedia, 2011)

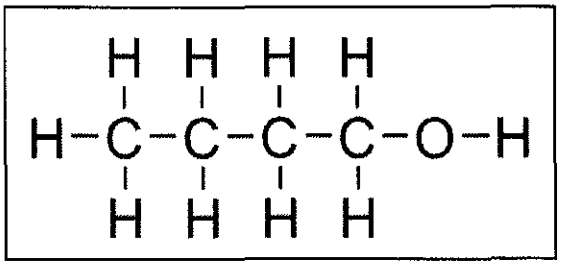

Figure 2.3: 1-butanol chain (Wikipedia, 2011)

A number of short chain alcohols have been shown to be effectively form bio-diesel from vegetable oil by acid catalysis. This approach, using methanol as the alcohol, however, has several noted shortcomings. In particular, it has been reported that these reaction take very long times approximately more than 69 hours with low conversion efficiencies (Freedman B. *et. al.,* 1984).

Comparative studies were conducted by Bradley D. Wahlen *et. al.,* (2008) have revealed that longer chain alcohol result in greater conversion efficiency under these conditions than do shorter chain alcohols. The most effective alcohol was n-butanol. He also have proved that, the efficiency of the reaction was found to increase with time for all of the alcohol. However, the methanol and ethanol reactions were found to result in very low conversion even after 16 minutes. In contrast, the n-propanol and n-butanol reaction efficiencies were much greater, achieving approximately 50% conversion over 16 minutes.

The molar ratio of n-butanol to fatty acid also play important role to achieve higher conversion. Bradley D. Wahlen *et. al.,* (2008) has conducted the optimization studies on ratio n-butanol to oleic acid, where he found that, even the lowest molar ratio of n-butanol to oleic acid (2:1) showed high conversion efficiency (>95%) within 4 minutes of reaction at minimum temperature of 110 °C.

The type of alcohol used in conversion of oleic acid to the alkyl ester also had effect on the efficiency of the reaction. Longer chain alcohols were found to result in greater efficiency when the reaction was conducted at 80 °C. Bradley D. Wahlen *et. al.,* (2008) said that, a likely explanation for this result is the increased miscibility of the longer chain alcohols is soybean oil. Both methanol and ethanol are marginally miscible with soybean oil, whereas the more hydrophobic n-propanol and n-butanol are much more soluble.

This was observed as two separate phases when methanol and ethanol were first mixed with the soybean oil following initial stirring. In contrast, n-propanol and n-butanol rapidly mixed with the soybean oil, forming a homogeneous solution (Mahfud F. H. *et. al.*, 2007). The speed of the chemical reaction is expected to be much faster for the homogeneous solution with the longer chain alcohols than the heterogeneous solutions with the shorter chain alcohols (Bradley D. Wahlen *et. al.,* 2008).

2.5.1 Affect of Long Chain Alcohol on Temperature, Alcohol Ratio and Reaction Time

Another benefit of using longer chain alcohols is that this allows for a higher reaction temperature to be used, because the boiling temperatures for the alcohol increase with chain length. Table 2.5 show the properties different for each alcohol.

Table 2.5: Properties differences of alcohol (Wikipedia, 2011)

Properties	Methanol	Ethanol	n-Propanol	n-Butanol
Molecualr formula	CH_4O	C_2H_6O	C_3H_8O	$C_4H_{10}O$
Molar mass ($gmol^{-1}$)	32.04	46.07	60.1	74.12
Density (gcm^{-3})	0.79	0.789	0.803	0.81
Melting Point (^oC)	-98	-114	-126	-90
Boiling point (^oC)	65	78	97	118
Viscosity (cP)	0.59	1.2	1.94	3

The ability to run trans-esterification reactions at higher temperature has a significant impact on the speed and efficiency of bio-oil. The higher reaction temperature achievable with the longer chain alcohols, coupled with improved miscibility of the alcohols with the hydrophobic oil triacylglycerides, also allows lower ratio of alcohol/fatty acid to be used (Bradley D. Wahlen *et. al.,* 2008). This will help for minimizing costs and the quantity of un-reacted materials in final product.

The stoichiometric minimum ratio of alcohol/triacylglyceride is 3:1 to allow for all three fatty acids on the triacylglyceride to be converted to alkyl ester. A 2:1 molar ratio of n-butanol/fatty acid was found to provide sufficient excess of alcohol to allow for high efficiency conversion to bio-diesel, resulting in minimal excess alcohol in the final product (Bradley D. Wahlen *et. al.,* 2008).

2.6 Taguchi L_9 Method

Prior to the emergence of Taguchi methods, factorial design of experiments was employed to investigate all the possible combinations of parameters that can fabricate the best product at certain costs. When the number of parameters is large, the factorial design approach faces four major drawbacks namely (Suzana Y. *et. al.*, 2010):

- It would be costly and time consuming to perform all the experiments;
- Completely different results may be obtained from two designs of the same experiment;
- Contribute of each parameter cannot be determined;
- Results may be difficult to be interpreted.

The Taguchi methods were developed to overcome these limitations by providing a systematic approach to the design experiments. Standard tables known as the orthogonal arrays are used to ease the design experiments and obtain consistent results from the same experiment.

2.6.1 Parameter Design

The aim here is to make a product or process less variable and more robust in the face of variation over which we have little or no control. An orthogonal array is abbreviated as L_N, where the subscript N refers to the number of trials that needs to be run for a given experiment. To be more descriptive, the number of levels and factors are included in a parenthesis next to the abbreviation of the orthogonal array. For example, L_4 (2^3) Taguchi method refers to using a four-trial orthogonal array to investigate the influence of three factors at two levels each on a given process.

There were 4 parameters that been consider under this experiment. Each one has 3 levels with the exception of production yield value. Using the array selector, the appropriate orthogonal array is L_9. At this stage, an optimum condition is determined at specific factor levels with or without the presence of uncontrolled factors. The third stage is tolerance design, which is used to fine tune the optimum

factor levels obtained from the parametric design stage. This is important to tighten the product quality, reduce both the capital and the operating costs, and increase customer satisfaction index at the same time.

CHAPTER 3

METHODOLOGY

3.1 Experimental Design

There are three kinds of variables tha must account for in an experiment. The independent or manipulated variable is what parameters that need to change in the experiment in order to observe the result. For this experiment, there were four parameters that will be change for each run. Those are:

- Ratio alcohol to bio-oil.
- Weight percentage of catalyst.
- Process temperature.
- Reaction time.

The dependent variable is end result that needs to be analyze, which is organic liquid product (OLP) production yield. The quantity of bio-oil use is the controlled variable which is fixed at 30 ml for each experiment.

3.1.1 Taguchi L_9 Method

Taguchi L_9 method was used for design the experiment based on selected independent variable. In order to run this method, special software called Design Expert version 8.0 (DE8) was used.

Figure 3.1: Icon for Design Expert version 8.0

After key in the data, nine runs of experimental design has been created base on orthogonal series. Those experimental designs are shown in Table 3.1.

Table 3.1: Experimental design based on Taguchi L_9

Run	Ratio alcohol to bio-oil	Reaction time (min.)	Temperature (°C)	Catalyst (wt%)
1	1:1	90	90	6
2	2:1	30	90	4
3	3:1	60	90	2
4	1:1	30	50	2
5	3:1	90	50	4
6	2:1	90	70	2
7	3:1	30	70	6
8	1:1	60	70	4
9	2:1	60	50	6

The production yields of each run were key in the DE8 and the analysis such as graph and statistical analysis were calculated automatically in the software.

3.2 Esterification Process

Overall exterification process can be simplified in Figure 3.2.

Figure 3.2: Process flow diagram for esterification process

3.2.1 Setup for Rotary Evaporator

The esterification processes were conducted using a rotary evaporator from BUCHI. Where some parameter has been set up constantly for every experiment such as the revolution of reactant flask per minute has been constant at 35 rpm and pressure inside the system at 55 mbar.

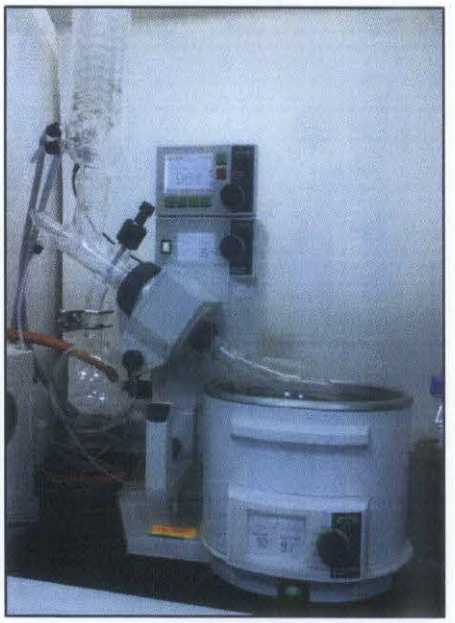

Figure 3.3: The rotary evaporator

The vacuum pump and water flow for condensation must be on before each experiment, in order to avoid any fault while conducting experiment. The samples were mixed in reactant flask. Reactant flask then was attached to it port and submerged in the water bath. Condensate products were collected inside the product flask. It is important to make sure that the glass equipment is clean before run for each experiment in order to avoid contaminant and to keep the purity of product.

3.2.2 Sample Preparing

Bio-oil was obtained from previous final year student, where it was process in local palm oil mill. 1-butanol and H_2SO_4 (95 – 97 wt %) was obtained from Merck Chemical. Quantity of bio-oil for every experiment was set constantly at 30 ml. Only the quantity of alcohol and weight percentage of acid catalyst was changed

according to each run design experiment. For each experiment, weight of 30 ml bio-oil and ratio alcohol was weighted in order to calculate the total weight of H_2SO_4 needed for each experiment. The calculation to calculate the weight percent of H_2SO_4 needed is as follow:

Total weight of sample including H_2SO_4 in flask, A (grams) =

$$\frac{(weight\ of\ bio-oil, g + weight\ of\ alcohol, g) \times 100}{(100 - x)}$$

Where x is the weight percentage of catalyst needed.

The quantity of H_2SO_4 needed is (grams):

A – (weight of bio-oil, g + weight of alcohol, g)

Then once the amount of H_2SO_4 has known, it was added to the mixture and stirs the mixture in order to make it homogenous.

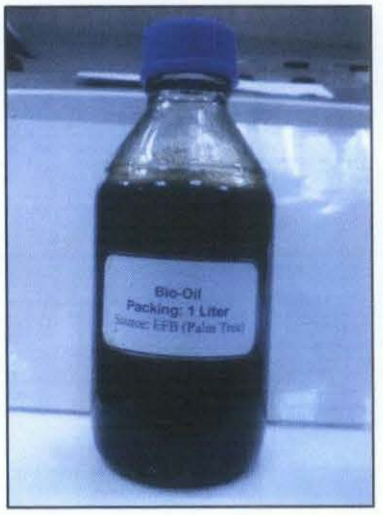

Figure 3.4: The crude bio-oil from empty fruit bunch

Figure 3.5: The homogenous mixture of bio-oil, 1-butanol and H_2SO_4

Then sample in the reactant flask was attached to rotary evaporator, and run under the process parameter.

3.2.3 Product Collection and Production Yield Calculation

Once the process is finish, the weight of OLP product in condense flask is weighted by using weighing machine. Then the water content in OLP was separated by using separator funnel. At first, let the OLP settle down for few minutes till there are two layers appear in the separator funnel. Then after water was separated from OLP, again the OLP and water separated was weighted and the production yield of OLP can be calculated.

Figure 3.6: Water separated from OLP using separator funnel

The production yield can be calculated as follows:

$$\% \text{ wt production yield} = \frac{Weight\ of\ OLP}{Weight\ of\ Bio-oil} \times 100$$

Once the optimum process has been identified, it was repeated for second time in order to confirm the production yield of OLP. From there the mean and standard deviation of process can be determined.

3.3 Characterization of Bio-Oil, OLP and Commercial Diesel

The characterization was conducted to bio-oil, OLP and commercial diesel in order to determine the properties difference of before and after esterification and with the commercial diesel. There were seven kinds of characterization and analysis that have been conducted to three samples.

3.3.1 pH Value

pH value was conducted by using pH meter from Mattler Toledo. The reason of conducting this analysis was to identify the acidity or alkalinity of sample.

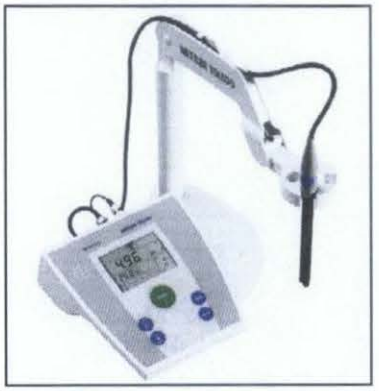

Figure 3.7: pH meter

3.3.2 Density and Specific Gravity Value

Both were measure using Anton Paar density meter. Density was measured to know the weight of sample in gram per volume and specific gravity is to know the ratio of the weight of a volume of the substance to the weight of an equal volume of the reference substance.

Figure 3.8: Anton Paar density meter.

3.3.3 Calorific Value

Calorific value also known as heat of combustion is the energy released as heat when a compound undergoes complete combustion with oxygen under standard condition. The chemical reaction is typically a hydrocarbon reacting with oxygen to form carbon dioxide, water and heat. The heat of combustion is conventionally measured with a bomb calorimeter.

The sample was weighted from 0.3 grams to 1.0 grams in the combustion glass, and places the combustion plate in the combustion chamber. Result was obtained after 20 minutes. The experiment need to be conducted twice for each sample in order to get the average value.

Figure 3.9: Bomb calorimeter

3.3.4 CHNS Analysis

CHNS analysis is elemental analyses of total carbon, hydrogen, nitrogen and sulphur was performed to provide carbonate and organic carbon and to get some idea of the composition of the organic matter.

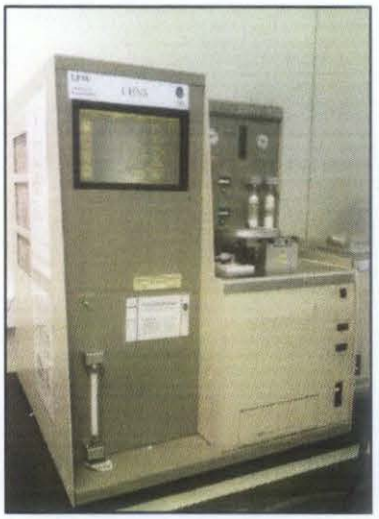

Figure 3.10: CHNS analyzer

3.3.5 Pour Point and Cloud Point

The pour point was analyzed to measure liquid lowest temperature at which it becomes semi solid and losses it's flow characteristics. The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as second phase giving the fluid a cloudy appearance. This term is relevant to several applications with differences consequences.

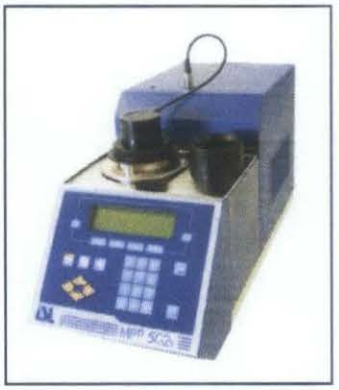

Figure 3.11: Fast, automated cloud and pour point model MPP 5Gs'

3.3.6 Gas Chromatography – Mass Spectrometry (GC-MS)

GC-MS is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within test sample. Specific tests need to be determined before send sample for GC-MS. For OLP the quantity of fatty acid butyl-ester need to be identified.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 The OLP Production Yield

This experiment were conducted to establish parameters that influence the conversion of bio-oil to bio-diesel using long chain of alcohol as solvent with present of H_2SO_4 as acid catalyst. In these studies, conditions were selected that resulted in maximization of the difference between variables as a way to probe the different conditions.

To evaluate the OLP yield, the OLP (wt %) phase was calculated after water being separated. Result and OLP yield wt % for each run is shown in Table 4.1.

Table 4.1: Result for each run

Run	Weight Before Reaction (grams)	Weight OLP (grams)	Weight liquid Separated (Grams)	Weight of Remained sample in flask (grams)	Production Yield (wt %)
1	56.49	17.34	13.84	3.61	30.7
2	80.54	36.76	13.86	1.86	45.64
3	**102.47**	**60.06**	**8.86**	**1.1**	**58.61**
4	54.26	8	9.93	0.89	14.75
5	104.41	20.59	10.76	6.79	19.72
6	76.98	32.99	13.35	0.16	42.86
7	106.02	43.68	8.63	13.42	41.2
8	54.69	19.22	13.58	2.1	35.15
9	81.23	13.22	7.58	11.55	16.27

Based on result in Table 4, the optimum condition to get higher yield of OLP is at run 3 where the process parameter were at temperature 90 °C, run for 90 minutes, with alcohol molar ratio was 3:1 and at 2 wt% of H_2SO_4.

Figure 4.1: The OLP after liquid separated

Figure 4.2: The remaining un-reacted sample in reactant flask

Experiment was conducted for second run at identified optimum condition, and result show constant production yield of OLP at 58 wt%. Thus it is prove that, at temperature 90 °C, reaction time 60 minutes, 2 wt% catalysts and molar ratio of alcohol to bio-oil is 3:1 was the optimum condition.

Table 4.2: Comparison of production yield at identified optimum condition

	Run 3 – 1st trial	Run3 – 2nd trial
Weight before reaction (grams)	102.47	103.91
Weight of OLP (grams)	60.06	61.12
Weight of water removed (grams)	8.86	4.21
Production yield (wt%)	58.61	58.82

By substituting the production yield in the Design Expert for Taguchi L_9, it shows that the optimum condition still same as in experiment.

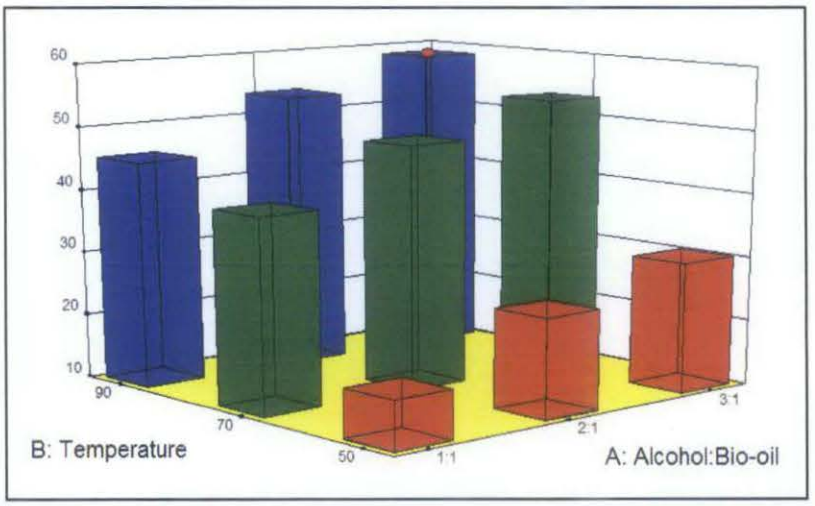

Figure 4.3: Design interaction between temperature and molar ratio of alcohol to bio-oil at 60 minutes of reaction time and 2 wt% of catalyst.

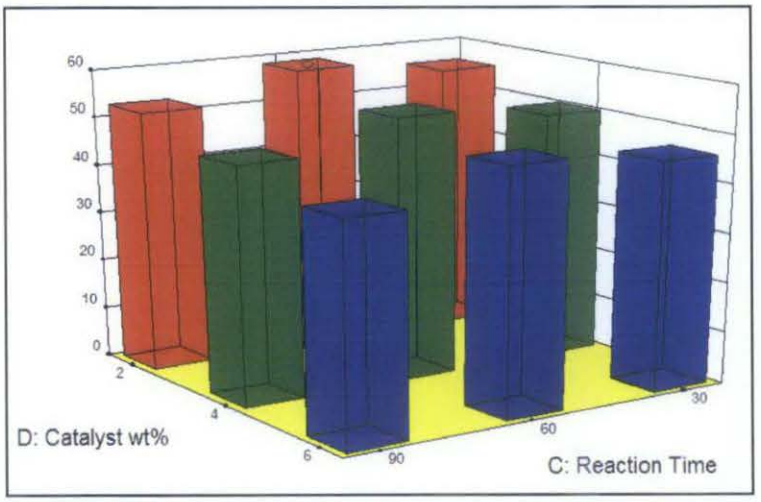

Figure 4.4: Design interaction between catalyst wt% and reaction time at ratio of alcohol to bio-oil 3:1 and at operating temperature of 90 °C.

From result we can observe that the high yield production of OLP was at the higher ratio of alcohol at the temperature of 90 °C. However, this ratio is considered low compared to the esterification process by using methanol or ethanol. By using the short chain of alcohol, the minimum amount of alcohol ratio is 30:1 in order to achieve >50 wt% of OLP (Bradley D. Wahlen *et. al.*, 2008). Some studies has shown that the minimum amount of n-butanol required to effectively esterify oleic acid was ratio at 2:1 and 4:1 but at temperature of 110 °C (Donato A. G. *et. al.*, 2008). This shows that the amount of n-butanol used in the experiment is low and this process can considered more economical compared to conventional method which is using methanol and ethanol.

Besides that, the catalyst wt% used in the experiment also gives effect to production of OLP. The highest production yield of OLP was using lowest catalyst concentration, which is at 2 wt%. Other than that, the water separated from run 3 and 4 and 6 which were used 2 wt% of catalyst showed lowest water separated from OLP. This proved that, by using acid catalyst the amount of water produce is less compare to based catalyst. The comparison study have been conducted and it is showed that total water produced for all 9 trials for using H_2SO_4 catalyst is less compared to using base catalyst which is calcium oxide (CaO). Which total water produce at acid catalyst is 6.42 wt%, while total water produce at base catalyst is 27.14 wt%.

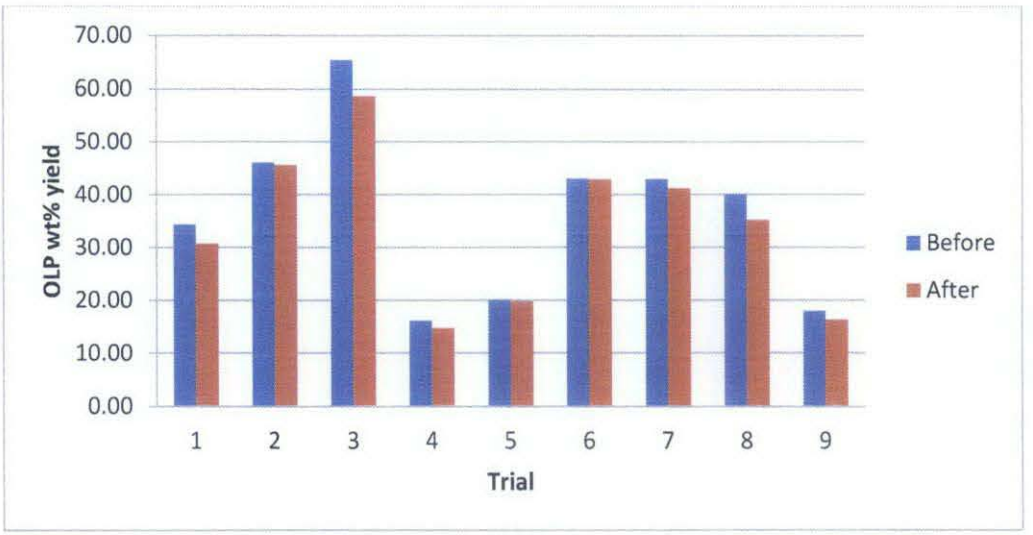

Figure 4.5: Comparison of OLP production yield on H_2SO_4 before and after water removal

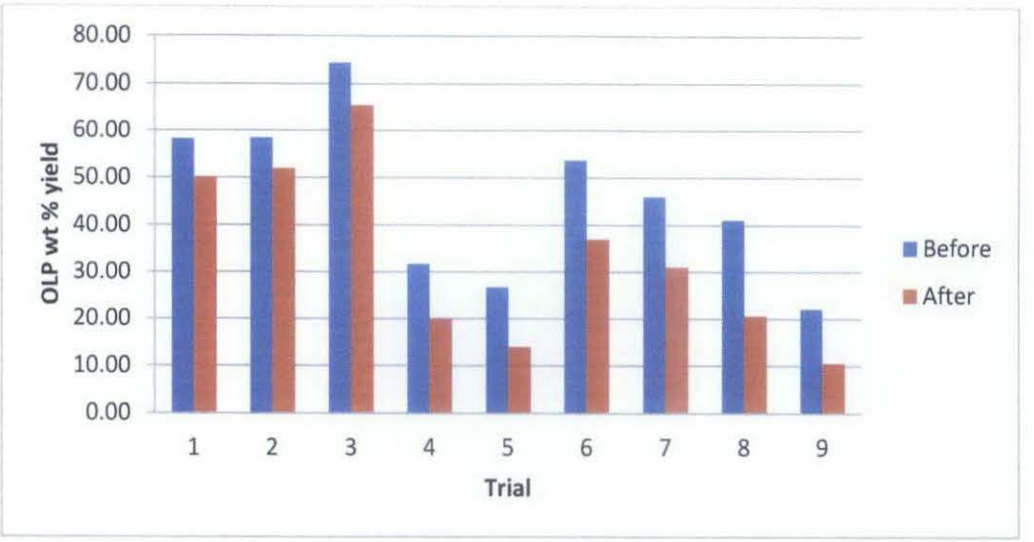

Figure 4.6: Comparison of OLP production yield on CaO before and after liquid removal

The effect of temperature also contributes to the production yield of OLP. The optimum temperature condition is between 70 to 90 ^{o}C. This might happen due to the selection of 1-butanol as solvent, because the boiling point of 1-butanol have higher boiling point. However the production of OLP is reduce when time is increasing. From data, the optimum reaction might happen between 30 to 60 minutes of reaction time.

4.2 Comparison of Properties of Bio-oil, Bio-diesel and Commercial Diesel

4.2.1 Comparisons of Physical Properties

The characterizations for each sample were conducted in order to observe and investigate the properties different for each sample. Data for physical properties for each sample is shown in Table 4.3.

An important characteristic of diesel fuels is the ability to autoignite, quantified by the cetane number and flash point. OLP has a higher flash point compare to commercial, meaning better and safer performance. The calorific value for OLP show it is half compared to commercial diesel value. This might due to the chemical compound in OLP that have other compound instead of alkyl ester alone.

Table 4.3: Comparison of physical properties of samples

Properties	Bio-oil	OLP	Commercial Diesel
pH	3.58	3.14	5.75
Density (kg/m^3)	1037.2	848.25	847.22
Specific Gravity	1.039	0.849	0.848
Calorific value (J/g)	-	28288	45671
Pour point (^oC)	-14	-13	-15
Flash point (^oC)	-	135	70

The lower heating value is the applicable measure. This is particularly due to production of OLP from bio-oil that has high hydrogen content that later produces much water. Other properties is quiet comparable except for the pH value. OLP have acidic reading, this might due to the usage H_2SO_4 as catalyst. The neutralization process needs to be done in order to increase the pH value, so it will not corrode the engine.

4.2.2 Comparisons of CHNS

The chemical properties of sample were determined by conducted the CHNS analysis. The result comparisons for each sample are shown in Table 4.4.

Table 4.4: CHNS comparison

CHNS	Bio-oil	OLP	Commercial Diesel
% Carbon	38	33.35	84.9
% Hydrogen	11	8.25	11.5
% Nitrogen	2.8	2.84	2.19
% Sulphur	0.44	0.4	0.6
% Oxygen (by different)	47.76	55.16	0.81

CHNS analysis for three samples shows that the carbons contain in OLP is 2.5 times lower than commercial diesel. Also the oxygen contain in OLP is 70 times more compare to commercial diesel. This shows that OLP later will be distillate to

produce butyl ester is more environmental friendly due to lower carbon contain. There will be less carbon release to atmosphere during combustion. Besides that, the high oxygen contain will enhance the combustion of bio-diesel. The nitrogen contain is slightly higher may due to the usage of nitrogen gas during pyrolysis of bio-oil as carrier gas.

4.2.3 Comparisons of GC-MS

4 samples were sent for GC-MS analysis. Those samples are the OLP, remaining sample in reactant flask; bio-oil and liquid remove from OLP.

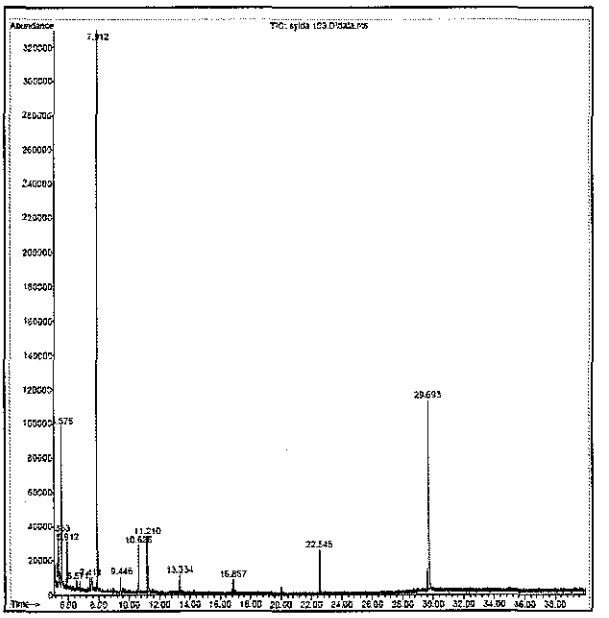

Figure 4.7: Chromatography for OLP

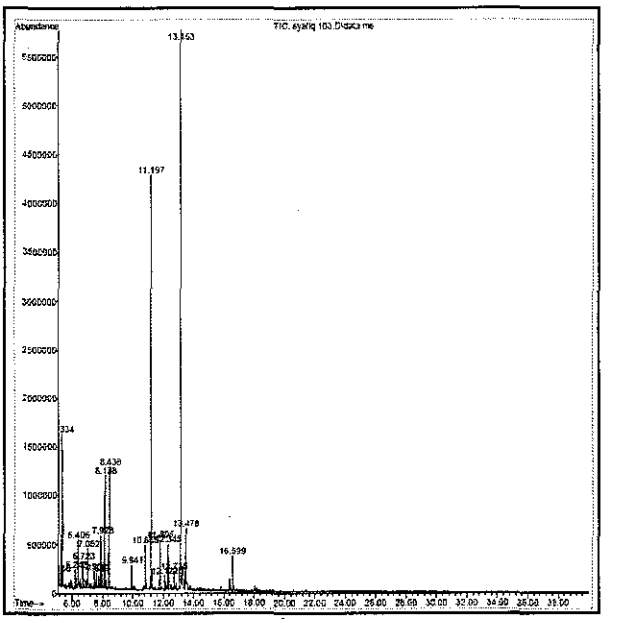

Figure 4.8: Chromatography for remaining sample in flask

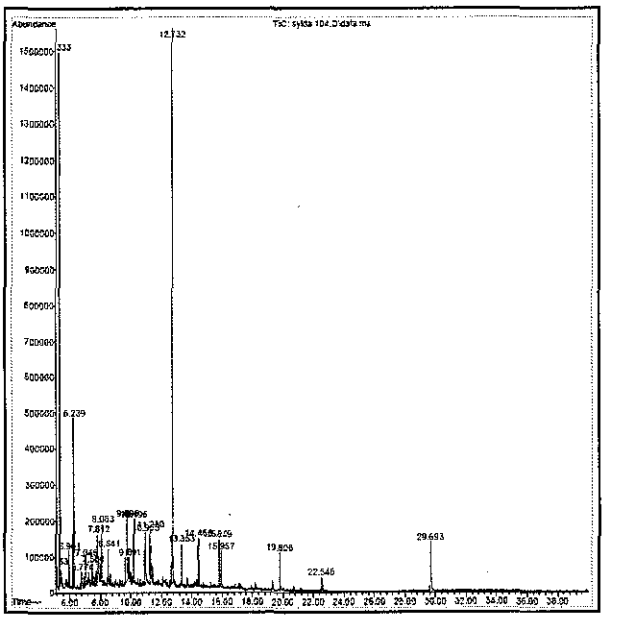

Figure 4.9: Chromatography for bio-oil from EFB

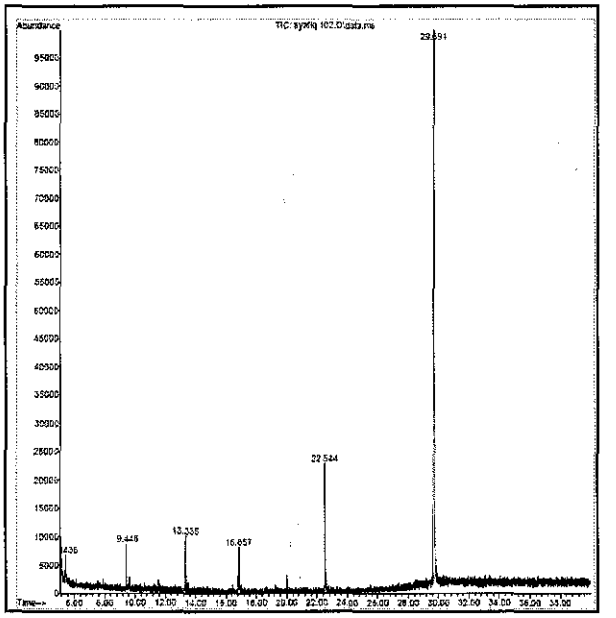

Figure 4.10: Chromatography for liquid removes from OLP

Based on GC-MS result, there are more than 70% conversions of alkyl ester group at optimum process. Where 40% is methyl ester, 28% is ethyl ester and 15% is butyl ester. This conversion is quite low compare to other study that shows the conversion of more than 95%. This may happen due to the temperature setting is low compare to other studies, where most if it run at 110 ^{o}C.

The composition of remaining sample show that the high quantity of H_2SO_4, which is 35%. It shows that most components already reacted and left the H_2SO_4 in the reactant flask. Some alkyl ester component also found in the remaining sample and surprisingly the number of methyl ester is quite high, amount of methyl ester found is 20%. This might happen due to reversible process of esterification. Where, some vapour may go back into the reactant flask.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Bio-diesel is an attractive alternative liquid transport fuel for a variety of reasons that have been articulated elsewhere. There are challenges to its widespread penetration into liquid fuel market; however, including cost and dependences on plant derived oils as feedstock. The optimum production yield of organic liquid product from esterification by using long chain alcohol was achieved at 58 %. This yield was achieved at parameter setting for molar ratio alcohol to bio-oil at 3:1, at 90 ^{o}C, reaction time at 60 minutes and 2 wt% of H_2SO_4. This method has shown that it is more economical where the ratio of alcohol used is low and the amount of acid catalyst use also at very low concentration. The water content of the bio-oil is reduced significantly and the value less were obtained using H_2SO_4. The reaction time also not too long compared because the optimum production was fall between 30 to 60 minutes of reaction time. The OLP produce also quite comparable to commercial diesel in term of physical and chemical properties. More over it is much safer because of it have higher flash point compared to commercial diesel.

This experiment should be conducted twice for each run in order to conduct statistical analysis such as Anova. Besides that, this experiment shall be conduct by using higher temperature but lower the boiling point of 1-butanol. Because Bradley D. Wahlen *et. al.* (2008) have showed that trans-esterification with n-butanol at 110 ^{o}C show great conversion of butyl ester which is 95% compare to 80 ^{o}C only have 50% of conversion. The process of neutralizing OLP is must in order to increase the pH value of OLP. This process might be conduct after esterication of acid catalyst and continue with trans-estrification process by using base catalyst.

In order to investigate the amount of butyl ester in OLP, the distillation experiment needs to be conduct. By conducting this study, the actual conversion of butyl ester from the process can be identified. GC-MS analysis is must, because only from this study, the actual amount of alkyl ester of fatty acid can be determined.

Without this data, the whole experiment can be question because there is no evidence to prove that OLP contain high quantity of fatty acid alkyl ester.

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